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A short review on polyaniline (PANI) based nanocomposites for various applications: enhancing the electrical conductivity

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Abstract. This short review has summarized the significance of polyaniline (PANI) advanced polymer that focusing into their modification strategy, electrical conductivity and various potential applications. PANI is one type of conductive polymer that was synthesized by oxidative aniline polymerization with varied concentration of acid dopant. In recent year, many researches has been conducted specifically to enhance the electrical conductivity of PANI. There have been numbers of studies involving PANI that specially reported the electrical conductivity could be improved through proper dopant (acid) selection and robust composite strategy. The PANI based nanocomposite shows higher electrical conductivity by integrating it with nanofiller due to the filler-matrix interface contact. Therefore, by modifying the PANI properties, it could be benefited for various potential application in the future.

1 Brief on PANI

Over the past decade, most research has emphasized the use of polyaniline (PANI) as an advance polymeric material due to its rich chemistry, high conductivity and good processing ability [1]. Recent developments in PANI research, has increased the need of conducting polymer utilization for the purpose of electron activity, semi conducting properties and electrical activity [2]. Therefore, PANI was increasingly recognized in various application such as solar batteries, anticorrosive coating, flexible electrode, storage devices and electromagnetic screen [3]. Basically, PANI was resulted from three oxidation states, known as completely reduced leucoemeraldine base, fully oxidized pernigraniline base and the emeraldine base, which consists of alternating oxidized and reduced repeat unit structure, as depicted in Fig. 1 [4]. Emeraldine base is very stable at room temperature

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and emeraldine salt are highly electrical conductive. While leucoemeraldine and pernigraniline are poor conductors [5]. There has been quantitative analysis of electrical conductivity of PANI that basically was influenced by their ability to transfer electrons. This paper seeks to remedy this issue by analyzing related literatures on the properties, synthesis and application of PANI for specific purposes. Moreover, due to current trend of integrating PANI with various functional fillers or nanofillers through robust composite strategy, PANI based nanocomposites was given special attention for this short review at the following section.

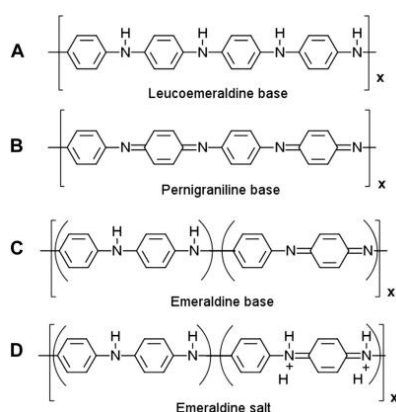


Fig. 1. Oxidation states of PANI, (A) the completely reduced Leucoemeraldine base, (B) the fully oxidized pernigraniline base, (C) the half oxidized-half reduced emeraldine base, and (D) the emeraldine salt [4].

2 The association between the synthesis and electrical conductivity of PANI

Previous researches has indicated that PANI can be synthesized by chemical or electrochemical processes. Electrochemical synthesis is the purest product which was free of admixture and does not require special procedure for purification [3]. The electrical conductivity properties of PANI are influenced by chemical and electrochemical redox reactions. Previous studies have reported that the conductivity values were increased by from $0.12 \times 10^{-3} \text{ Scm}^{-1}$ to $0.13 \times 10^{-3} \text{ Scm}^{-1}$ for the use of sulfonic aminophenol dopants [6]. Other studies have considered the relationship between the synthesis of PANI by using sulphuric acid which shows better electric conductivity compared than nicotinic acid (NA) and 2-methylnicotinic acid (MNA), due to large dopant size in polymeric matrix [7]. Similarly, Wang et al. (2017) found that the measured conductivity values of Molybdenum disulfide (MoS_2)/PANI nanocomposites shows an enhancement from $1.09 \times 10^{-1} \text{ Scm}^{-1}$ to $2.50 \times 10^{-1} \text{ Scm}^{-1}$ due to effects of dopant used. These values have increased with increasing amount of MoS_2 [8].

However, among the dopants used, fluorine doped tin oxide (FTO) shows the highest value of electrical conductivity readings reached into 4.76 Scm^{-1} for 3.00 mg of dopant weight. The electrical conductivity of PANI had decreased as the weights of dopant was decreased [9]. This result has supported further the hypothesis for the electrical properties of PANI which are a function of synthesis condition either oxidation or protonation. The following Table 1 provides the summary of synthesis methods using different types of dopants to give different results in term of their electrical conductivity. It was found that the

selection of acid based dopant are crucially significance in influencing the big gap different of the resulted electrical conductivity of PANI.

Table 1. The acid dopant agent against the electrical conductivity of PANI.

Ref.	Synthesis method	Dopant	Sample	Conductivity (S cm^{-1})
[6]	PANI	aminophenol sulfonic	PANI co-polymer	0.12 $\times 10^{-3}$ 0.13 $\times 10^{-3}$
[7]	PANI/H ₂ SO ₄	sulphuric acid nicotinic acid 2-methylnicotinc acid	PANI/H ₂ SO ₄ PANI/NA PANI/MNA	1.09 0.63 0.089
[8]	MoS ₂ /PANI	molybdenum disulfide	PANI MoS ₂ /PANI-8 MoS ₂ /PANI-38	1.09 $\times 10^{-1}$ 2.50 $\times 10^{-1}$ 2.38
[9]	FTO/PANI-GR	fluorine doped tin oxide (FTO)	FTO/ PANI FTO/PANIGR 1 mg FTO/PANIGR 3 mg	0.09 0.454 4.76

3 Nanofiller for PANI based nanocomposites

Over the past decade, most research in nanotechnology has emphasized the investigation on polymeric based nanocomposites. The manipulation of molecules in one dimension is about 1 to 100 nanometers (nm) that are available in nanocomposite. There are various types of nanofillers used such as clay nanoparticles [10], silver nanoparticle [11], oxide nanoparticles [12], graphene nanoplatelets [13] and carbon nanotubes [14]. Recent development in PANI research has confirmed the need to incorporate PANI with varies nano-fillers that may resulting in higher performance and good feature advantages for ideal generation of future energy storage devices [15]. Chatterjee et al. (2011) has demonstrated that the electrical conductivity has increased by adding the optimum nanofiller content. Electrical percolation could be achieved in the composites at between 1.50 – 2.00 wt% of nanofiller loadings, as clearly depicted in Fig. 2 [16]. It was presented that, different type of nanofillers would possessed different value of electrical conductivity when it was incorporated into PANI polymers at different amount of nanofiller loadings.

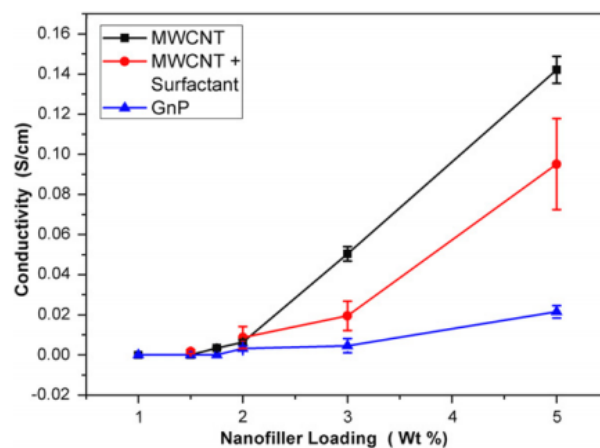


Fig. 2. Difference nanofiller Multi-wall carbon nanotubes (MWCNTs) and Graphene Nanoplatelets(GNPs) for electrical conductivity response.

Studies conducted by Jelmy et al. (2013) shows the produced polymer nanocomposites samples with nanofiller exhibits higher electrical conductivity. For instance, by adding Carbon Nanotube's CNTs into PANI has yielded about 2.28 Scm^{-1} , Carbon Black (CB) about 0.03 Scm^{-1} and graphite about 0.07 Scm^{-1} as compared than PANI sample, without nanofiller addition of 0.007 Scm^{-1} [15]. Similarly, Imran et al. (2018) has found that the electrical conductivity of PANI-GNPs had increased steadily with increasing of GNPs loading, which are $2.00 \times 10^{-4} \text{ Scm}^{-1}$ (1.00wt%) and $3.16 \times 10^{-2} \text{ Scm}^{-1}$ (2.00 w%) respectively, as compared to pure PANI $4.38 \times 10^{-17} \text{ Scm}^{-1}$ [13]. Other studies also have considered the relationship between filler and electrical conductivity. It shows that Multi-wall carbon nanotubes(MWCNTs) nanofiller shows higher electrical conductivity as compared than pure PANI due to charge transfer effect from the quinoid rings of the PANI to the (MWCNTs) [17]. The most striking result to emerge from the data is that, the electrical conductivity of PANI sample filled by CNTs and Graphene(GN) shows the higher value of conductivities than PANI without filler [17]. As an output, the usage of carbon based nanofillers provides various potential applications depending on the appropriate electrical conductivity function. Overall, this result has indicated that the use of carbon based nanofiller was beneficial to influence the electrical conductivity of PANI. Debate has continues about the various application of PANI in term of electrical conductivity function.

Table 2. The Variable PANI System and nanofiller against reaction of Electrical Conductivity.

Ref.	PANI System	Filler	Sample	Conductivity (Scm^{-1})
[13]	PANI PANI/GNP	unfilled GNPs	PANI PANI-GNP 1.00wt% PANI-GNP 2.00wt%	4.38×10^{-17} 2.00×10^{-4} 3.16×10^{-2}
[15]	PANI PANI/CB PANI/GR PANI/MWCNT	unfilled carbon black (CB) graphite (GR) MWCNT	P-H ₂ SO ₄ PCB PGR PCNT-H ₂ SO ₄	0.01 0.03 0.07 2.28
[17]	PANI/MWCNTs	unfilled MWCNT	PANI PANI-CNT	0.50 1.95
[18]	PANI PANI/CNT PANI/GN	unfilled CNT GN	PANI PANI/ CNT PANI/GN	0.70 6.80 1.50

4 Application of PANI based nanocomposites

Conducting polymer in energy application has gaining special attention due to large specific capacitance properties. Questions have been raised about the limitation usage of PANI in engineering applications due to its unstable condition at neutral pH and at higher temperature. However PANI belongs to the organic conductive electro active polymers, where under ambient conditions may possessed electrical conductivity and the features are suitable to electrochemical storage application [19]. There was a large scale of published studies describing the utilization of PANI in electrical conductivity related applications such as transparent antistatic coating [20], semiconducting properties like solar batteries [21] and electrical activity for example, electrodes supercapacitor [22] and anticorrosive coating [23]. This has been summarised in the following Fig. 3.

PANI have been identified as major contributing application for increased of many electrical purposes and useful ways to suppress electrostatic charging. This conducting polymer have advantages in various fields such as for electrode material due to the nature

of active material in energy storage application [22]. However, some disadvantages may include PANI electrode fragility and structural degradation under the harsh environments. A considerable amount of literature has been published regarding advantages and disadvantages of PANI in potential application of transparent antistatic coating [20], anticorrosive coating [23] and solar batteries [21], as summarized in the following Table 3.

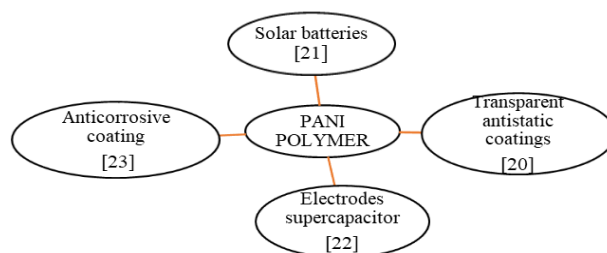


Fig. 3. The variable application of PANI in electron conductivity, semiconducting properties and electrical activity

Table 3. Various PANI application, advantages and disadvantages of PANI system against the electrical conductivity function.

Ref	PANI system	Potential Application	Advantages	Disadvantages
[20]	PANI/acrylic	transparent antistatic coatings	nanocomposite film is flexible	expensive
[21]	PANI-SnO ₂ (Tin Dioxide)	solar batteries	higher efficiency under UV light irradiation	predominant factor for the photocatalytic activity
[22]	PANI/Graphene	electrodes supercapacitor	ability to deliver higher power density than rechargeable batteries	obtain both high power and energy density
[23]	PANI-An/G (Modified graphene)	anticorrosive coating	prevents the path surface of the substrate from being corroded	extent limits of anti-corrosion performance.

5 Durability and future development on PANI

Recently, simpler and more rapid test in the durability and consistency of PANI in terms of conductivity has been developed. Although substances can produce materials with high conductivity values, but their use at longer period of time should be noted. The Studies show the important of doped with phosphoric acid (PANI-PA) is capable of forming a protective oxide layer on the surface of the material that prevents the diffusion of corrosive ions [24]. Factor found to be influencing have been explored in several studies. In 20000 cycles, ionic and electronic resistances of PANI-based electrochemical was increased and show good charge capacity value of only 5% loss [25]. In addition, the nanostructure also proved to be effectively exhibited better properties. the next study should focus on the unique nanostructure of the electrical conductivity field [26]. Previous research has indicated that, in further work PANI needs to be designed in tailor-made derivatives for advanced performance in supercapacitor application [27]. PANI when combined with 3-D

porous scaffolds can produce medium for transmission of myocardial infarct [28]. For the future development, the addition PANI has stability of conductivity value and electricity power at longer period of time.

6 Conclusions

In overall, the electrical conductivity of PANI has generally influenced by at least two important aspects which are the dopant agent and the nanofiller used. As the matter of fact, from this short review, PANI with dopant agent has shown increased of their electrical conductivity as compared than PANI without dopant addition. It has proven to be effective that the electrical conductivity was increased with the increase of dopant concentration. In another hand, the application of carbon based nanofiller not only shows the higher resulted electrical conductivity of PANI. In addition, due to the ability to modify the electrical conductivity of PANI through the utilization of acid dopant and carbon based nanofiller, has opened up various potential application for PANI based conductive polymer. However, it can be said that, this situation only can be achieved if the optimum amount of acid dopant and nanofiller added could be accurately determined.

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